The Atomic Weight of Radium.

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(Received December 27, 1911,—Read February 8, 1912.)

The essentials in determining the correct equivalent of an element are :—

(1) A pure compound of the element, and sufficient evidence of purity.

(2) An advantageous transformation, in which the weight of the element or elements combined with the one of which the equivalent is to be determined is as large as possible.

(3) If possible, no transference, and no operation which necessitates the use of reagents which can convey into the solution matter which may be adsorbed.

(4) A quantity sufficient in amount to make it possible with the balance at disposal to determine its weight to at least 1 part in 20,000.

(5) Resistant vessels, which will not themselves give up any material to the substance, and so make its purification difficult.

Determinations of the equivalent of radium have been made by Madame Curie, by Sir Edward Thorpe, and by O. Hönigschmid. Madame Curie's first determination, made in 1902, may be taken as avowedly only a rough approximation. Using 90 mgrm. of chloride, she found the atomic weight to be 225, assuming, no doubt with justice, that radium is a dyad.* Her second determination, of which a short account is given in the 'Comptes Rendus' for 1907, August 19, and a complete one in 'Le Radium,' translated in full in the 'Jahrbuch der Radioactivität,' 6, p. 38, employed the same method, viz., precipitation and weighing of silver chloride from a known weight of anhydrous radium chloride.

Madame Curie, in her earlier work, proceeded to the ultimate atomic weight progressively, raising the number from 140 to 146, then 174, then greater than 220, and in 1902 to 223·3; finally, with 90 mgrm., she obtained the figures 225·5, 226·0, and 224·2; mean, 225·2, which she regarded as accurate within a unit.

The method of crystallisation described in her later paper is merely indicated. A solution of radium chloride in hydrochloric acid was employed; 0·55 grm. was dissolved and evaporated, and deposited needle-shaped crystals. "The crystallisation was continued until almost all the salt had separated; the preparation was allowed to cool; the mother-liquor, containing very little salt (1 to 2 mgrm. in several cubic centimetres of the solution) was poured off. I carried out a large number of such operations, and always put together the separated portions. The salt was then divided into two parts, a first and a last portion." The samples were then tested spectroscopically for barium. She next added alcohol to a very concentrated aqueous solution until the salt was *completely* separated (italics ours). The liquid was then poured off and added to the mother-liquor. In this manner she obtained a certain improvement; it is not obvious, however, why an improvement was effected, if the salt was *completely* precipitated.

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* 'Comptes Rendus,' July, 1902, and 'Ann. Ch. Phys.,' 1903, vol. 30.

The silver chloride was filtered off, dried, ignited, and weighed on a balance sensitive to 0·05 mgrm. The amount taken was about 0·40 grm. After deducting the weight of the filter-ash, the figures 226·62, 226·31, and 226·42 were obtained, the values for Ag = 107·93, and Cl = 35·45 having been taken. Substituting 107·88 and 35·46, the figures are less by 0·09, or 226·53, 226·22, and 226·33; the mean of these is **226·36**.

Madame Curie comments unfavourably on crystallisation of the bromide; she states that the bromide, being much more soluble than the chloride, lends itself less easily to crystallisation, and that it is unstable, and changes very quickly; we shall see that these remarks are inapplicable. She also states that it is impossible to prevent a deposit of radium sulphate; this we have not noticed, having taken reasonable care to keep the vessels covered. She was also troubled by the impurities in the distilled water and the hydrochloric acid which she used, even though they were specially prepared and kept in platinum bottles. The silver chloride was always radioactive and luminescent; but Madame Curie states that it contained no radium detectable by the balance.

In his Bakerian Lecture for 1907,* Sir Edward Thorpe described experiments on the equivalent of radium. His raw material, placed by the courtesy of the Austrian Government at the disposal of the Royal Society, was "about 500 kgrm.," or, say, half a ton, of pitchblende residues from Joachimsthal. These residues were delivered by the Austrian Government to M. Armet de Lisle in Paris for preliminary extraction. Thorpe remarks: "The residues, as received by M. Armet de Lisle, were stated to have a radioactivity of about two and a half times that of uranium." This corresponds with Madame Curie's experience, for she wrote†: "La pêcheblende que nous avons analysée était environ deux fois et demi plus active que l'uranium." The total radioactivity of the 500,000 grm. received by M. Armet de Lisle was thus equal to that of

$$500{,}000 \times 2{\cdot}5 = 1{,}250{,}000 \text{ grms. of uranium.}$$

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* 'Roy. Soc. Proc.,' A, vol. 80, p. 298.

† 'Comptes Rendus,' vol. 127, p. 176.

Thorpe received from Paris 413 grm. of mixed chlorides of barium and radium, the radioactivity of which was 560 times that of uranium. Hence the 413 grm. had a total radioactivity equal to that of

$$413 \times 560 = 232{,}000 \text{ grms. of uranium.}$$

Taking the radioactivity of pure radium chloride as equal to 1,800,000 times its weight of uranium, the figures result:—

Delivered in Paris ...... $\dfrac{1{,}250{,}000}{1{,}800{,}000} = 694$ mgrm. of pure radium chloride.

Received in London ... $\dfrac{232{,}000}{1{,}800{,}000} = 129$ " "

The method of separation of radium and barium followed by Thorpe was "substantially the same as that adopted by Madame Curie"; 9400 recrystallisations of the chlorides were carried out, towards the end in silica vessels. No details are given of the methods of crystallisation. The analytical process was also identical with that employed by Madame Curie, namely, precipitation of silver chloride from the dissolved radium chloride, acidified with nitric acid, subsidence, washing with distilled water six times, drying at 160°, and weighing on an assay balance sensitive to 0·1 mgrm. With the quantities used, an error of 0·1 mgrm. in the weight of the silver chloride made a difference of no less than half a unit in the atomic weight. The atomic weights used, moreover, viz., Cl = 35·45, and Ag = 107·93, have now to be corrected to 35·46 and to 107·88, hence the results of Thorpe's determinations are:—

I. 226·7; II. 225·6; III. 227·6.

The first two results were determinations with the same sample, which was recovered for the purpose; the last determination was made after mixture of another portion of 24 mgrm. with the first 64; this mixture was "repeatedly crystallised"; and the final results yielded a higher atomic weight. That the method employed was not particularly advantageous is shown by the discrepancy between determinations I and II, which, so far as weighings are concerned, should have differed by not more than 0·5 unit; that finality had not been reached is, we think, clearly shown by determination III, when, after repeated crystallisations, the atomic weight has been raised by one or by two units.

It is also stated by Thorpe that the bromide loses bromine, and eventually becomes insoluble in water, and that radium chloride, after standing in contact with glass, gives a faintly turbid solution; indeed, that all vessels are attacked by it, forming, apparently insoluble silicates. "A similar observation has been made by Madame Curie."

A new set of determinations has been made by O. Hönigschmid,* in which quantities somewhat exceeding 1 grm. were used. The method of purification was again that employed by Madame Curie and Thorpe, viz., repeated crystallisation of the chlorides from hydrochloric acid, and precipitation of the aqueous solution of the salt with alcohol. The equivalent was not altered after 50 such crystallisations and 13 precipitations with alcohol, and that material was regarded as pure, and employed in the final determinations. The method, too, was the same as that described, but in two cases the chloride of silver was reduced, and the weight of the silver ascertained. The mean result, taking $Cl = 35{\cdot}46$ and $Ag = 107{\cdot}88$, was 225·95; the extremes in seven determinations were 225·92 and 225·97.

Hönigschmid's work is undoubtedly very well done; the only doubt is whether his material was perfectly pure. It has been shown by Guye that it is impossible to separate potassium chlorate from potassium chloride, however many times the chlorate is recrystallised, owing to the existence of a solid solution. It will be seen in the sequel that the number obtained by Hönigschmid must be regarded as a minimum result.

Whilst these researches show the approximate atomic weight of radium, it cannot be said that the results must be accepted as final, for they are lacking in several of the conditions stated at the beginning of this paper. There is the possibility of contamination of the solutions with the reagents used; transference was necessary in all the experiments; both Madame Curie and Sir Edward Thorpe were troubled with insoluble deposits; and the accuracy of weighing was in the former case only 1 in 8000, and in the latter only 1 in 700. These disadvantages were absent from the method which we employed, viz., the conversion of radium chloride into radium bromide by heating it in a current of hydrogen bromide, and *vice versâ*; there was no transference, and only gaseous reagents were used.

By the courtesy of the Radium Corporation, 330 mgrm. of anhydrous radium barium bromide, containing about 70 per cent. of radium bromide, was placed at our disposal. This material, after being extracted from pitchblende, had been precipitated as sulphate, thus removing all heavy metals except lead, barium, and radium. The sulphates were delivered to us as bromides, into which they had been converted. The bromides received were dissolved in water and treated with sulphuretted hydrogen, which gave a small black precipitate; this was removed by settling and pipetting off the clear liquid, adding distilled water, again settling, and so on, until the precipitate had been thoroughly washed. Sulphuric acid was then added to the solution, so as to precipitate barium and radium. This precipitate was thoroughly washed by decantation; traces of alkalies, if present, were thus removed. All these operations were carried out in silica vessels. The washed and dried sulphates were next heated to redness in a mixture of carbon tetrachloride vapour and gaseous hydrogen chloride; they were thus converted into chlorides. A trace of iron appeared to be removed at this stage, and the residue became brilliantly white. The mixed chlorides dissolved completely in water, showing the absence of silica, and also of thorium, which volatilises as chloride under the circumstances. The Cornish pitchblende, however, contains only a few grammes of thorium per ton of uranium, and the maximum amount of mesothorium and radiothorium would therefore be vanishingly small.

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* 'Anzeiger der Akademie der Wissenschaften in Wien,' October 19, 1911; 'Sitzungsberichten der Akademie der Wissenschaften in Wien,' November, 1911.

These chlorides were next converted into bromides by heating to redness for some hours in a current of hydrogen bromide, and the exact amount was determined by conversion into chloride and back again into bromide in the following manner:—

The material was transferred without loss into a light silica capsule, resembling in form and capacity a No. 00 porcelain crucible, weighing on an Oertling's assay balance 1086·18 mgrm. A displacement of the milligramme rider on the beam of 1/50th of its length, corresponding to 1/50th of a milligramme, gave on the pointer-scale a difference of one division; greater accuracy could have been attained, but was not desired. The weights were Oertling's "assay silver weights."

It had been repeatedly proved that the weight of such a silica capsule remains absolutely constant even after it has been heated to redness for some hours in a current of dry gaseous hydrogen chloride, charged with the vapour of carbon tetrachloride; such a mixture of gases is easily made by use of a Kipp containing lumps of solid ammonium chloride and concentrated sulphuric acid. The gas, after passing a column of phosphoric anhydride, bubbled through a U-tube containing carbon tetrachloride. From this it entered a silica crucible of peculiar form, best illustrated by a figure which explains itself (fig. 1). The stopper is ground in, and it may be removed to introduce or take out the silica capsule. The silica apparatus was made by the Silica Syndicate, of Hatton Garden.

Heating in this mixture of gases removes all volatile chlorides; it also converts sulphates of the alkalies and alkaline earths into chlorides, and is by far the easiest way of effecting that conversion quantitatively. A very good equivalent was found for barium by conversion of a weighed amount of sulphate into chloride in this manner; the resulting chloride dissolved without a trace of residue. The radium bromide was thus converted into chloride; it was then reconverted into bromide by substituting for the hydrogen chloride plus carbon tetrachloride gaseous hydrogen bromide, made by bubbling hydrogen through bromine, passing the mixed gases through a red-hot silica tube charged with asbestos, and then through a column of phosphoric anhydride. The hydrogen bromide then entered the silica crucible; it converted the chloride into bromide. This operation takes about three hours.

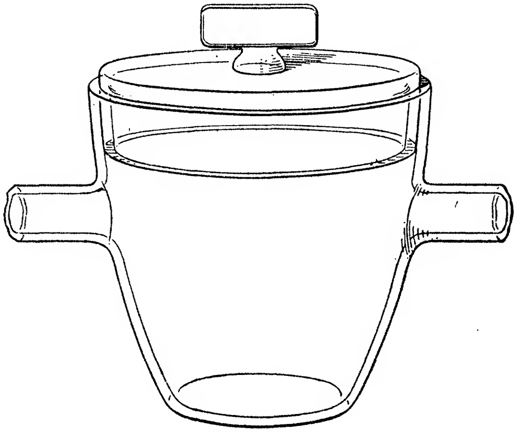

FIG. 1.

When the crucible cools, the mixture of bromides begins to shine with a beautiful sky-blue phosphorescence, increasing in intensity as it cools. The chlorides show a darker blue colour, and rapidly turn black. The silica capsule, while still fairly hot, was removed with platinum forceps and placed in a weighing bottle, arranged as a desiccator, with fragments of caustic potash. After standing for an hour it was weighed on the assay balance. Much has been said regarding the hygroscopic nature and the easy transformation of the bromide into insoluble substances, and there is some truth in the remarks. But in actual fact, it is not very hygroscopic. It is easy to transfer the capsule to the pan of the balance; and moisture is practically excluded by covering the capsule with a slip of mica during the operation of weighing. It stands to reason that the weight of the total moisture contained in the air imprisoned in the capsule is almost if not quite negligible; and even if withdrawn by the anhydrous bromide during the operation of weighing there is no reason why it should enter from the balance case. We have found, in effect, that under the circumstances the weight remains constant for more than an hour.

Having weighed the mixed bromides of barium and radium they were converted into chlorides by heating in a stream of dry hydrogen chloride, prepared as already described; this change is more rapid than the conversion from chloride to bromide. The capsule and contents were then weighed. A second conversion from chloride to bromide was made, and the weight again ascertained. The actual weights were as follows:—

Weight of capsule and mica cover................. 1086·18 mgrm.
„ mixed bromides, 1416·82 − 1086·18 = 330·64 „
„ „ chlorides, 1332·14 − 1086·18 = 245·96 „
„ „ bromides, 1416·82 − 1086·18 = 330·64 „

If $x =$ weight of $RdBr_2$, and $y-x$ that of $BaBr_2$, and $297{\cdot}32/386{\cdot}24 = RdCl_2/RdBr_2$, and $208{\cdot}29/297{\cdot}21 = BaCl_2/BaBr_2$, then when $y = 245{\cdot}96$,

$$(297{\cdot}32/386{\cdot}24)x + (330{\cdot}64 - x)(208{\cdot}29/297{\cdot}21) = 245{\cdot}96,$$

whence

$$x = 206{\cdot}53 \text{ mgrm. } RdBr_2 \quad \text{and} \quad 330{\cdot}64 - 206{\cdot}53 = 124{\cdot}11 \text{ mgrm. } BaBr_2.$$

Suppose that the chlorides had weighed 0·1 mgrm. less than 245·96, the difference in weight of the anhydrous bromide would have amounted to 205·08 instead of 206·53, or 1·45 mgrm. less. The balance can be trusted, however, to register one-fifth of this difference, or 0·3 mgrm. The percentage of radium bromide in the mixture is 62·5. This experiment is merely cited to show how it is possible to estimate the relative weights of radium and barium bromides in a mixture.

This mixture was dissolved in water in a silica capsule, and left to evaporate over night in a vessel containing phosphoric anhydride. In the morning a scum of carbonate had formed on the top. Addition of a drop of hydrobromic acid, made by saturating with hydrogen bromide water trebly distilled in silica and contained in a silica test-tube, dissolved the carbonate with effervescence to a clear solution.

The method of evaporating and crystallising was as follows:—The capsule containing the solution was placed in a flat-bottomed silica basin over a water-bath; evaporation proceeded until flat crystals began to form on the side of the capsule. These were pushed back into the liquid with a platinum wire, and evaporation was continued until a fair amount of crystals had separated. The solution was then allowed to cool, and the mother-liquor was removed with a small silica pipette of the shape and size shown in the figure into a silica capsule, also shown (fig. 2).

The crystals were re-dissolved in about six drops of water, which, like all the water used, had been distilled from silica, the steam passed through a short length of silica tubing, packed with silica wool and heated to redness. This prevented any carrying over drops of undistilled water. The water was kept in a little silica washbottle, entirely constructed of silica, without corks or rubber, from which it was easy to expel a single drop without splashing. All these operations were carried out in a glass photographic tray, covered by a sheet of plate-glass when it was not required to open it. In this way dust was practically excluded.

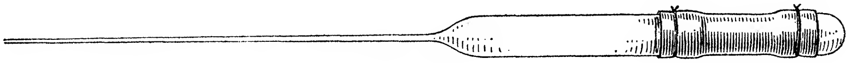

Fig. 2a.

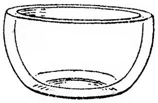

Fig. 2b.

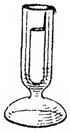

Fig. 2c.

The capsule with its six drops of water was heated in the silica basin over the water-bath until the crystals had dissolved. Two drops of hydrobromic acid were then added, and the evaporation continued as before; the second mother-liquor was placed in capsule 2; exactly the same manipulations gave mother-liquors 3 and 4.

At this stage a sample was taken from the residual crystals in the capsule, which may be called 5; it was transferred to a small silica bucket, weighing about 30 mgrm., contained in a holder of silica, as in fig. 2c, and it was heated to redness in the silica crucible (fig. 1) for an hour, in a current of hydrogen bromide. It was then transferred to a small weighing-bottle desiccator, and stored over potash for an hour. The bucket was then hung on the balance, and, after being weighed, the bromide was converted into chloride in the manner described, by heating for several hours in a current of dry hydrogen chloride; it was then cooled in the desiccator and weighed. It was then re-converted into bromide by heating it in a current of hydrogen bromide until weight became constant. The first weighing as bromide was rejected.

The weights are as follows:—

Weight of chlorides...............	0·42188	mgrm.
„ bromides...............	0·55082	„
Difference	0·12894	„

The atomic weight, calculated by the equation

$$0{\cdot}12894x = (159{\cdot}84 \times 0{\cdot}42188) - (70{\cdot}92 \times 0{\cdot}55082),$$

where 159·84 and 70·92 are respectively Br_2 and Cl_2, is 220; the percentage of radium bromide in the mixture of bromides, on the assumption that the atomic weight of radium is 226·4, has thus been raised from 62·5 to 94·4 per cent.

It is advisable here to introduce a short description of the balance, which, though essentially similar to that already described by us,* was slightly modified to suit the new requirements. In the experiments on niton, the measurement of a very small difference in weight (about 1/1000 mgrm.), with an accuracy of the order of 2 per cent., was required; but in the present work such an extreme sensibility was not necessary, although a much greater percentage accuracy was essential. The instrument was accordingly modified, so as to carry a much greater load, and the beam was made of a very rigid form. The design is shown in the diagram (fig. 3).

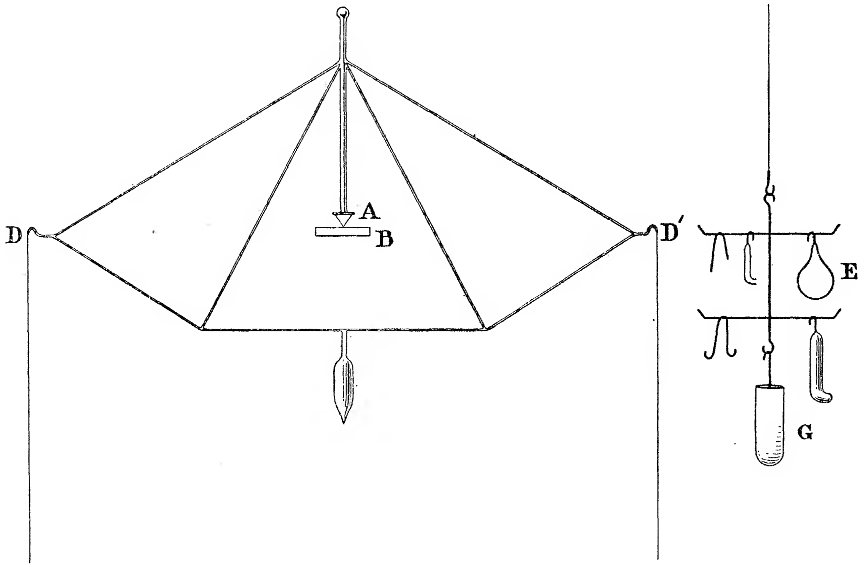

Fig. 3.

A is a central compound knife-edge, consisting of two small silica prisms, resting on a plate B of polished quartz. The arms carried two silica fibres at DD′, sealed on so that the points of attachment were as nearly as possible in the same plane as the edge A. The fibres terminated in hooks supporting a small framework of silica, on which the vessel to be weighed, the weights, and the counterpoise-bulb were suspended. The air-tight case and the attachments were similar in all respects to those described by Steele and Grant, and need no special mention. Previous experience with the more sensitive balance showed the importance of weighing at low pressure, in order to avoid air-currents produced by temperature changes when the case is suddenly filled or evacuated. This restriction of the range of pressure set a limit to the weight which could conveniently be applied by the counterpoise-bulb, and necessitated the use of a set of weights, for weighings of high percentage accuracy. The balance was therefore constructed so that its constant load was made up of: (*a*) the counterpoise-bulb; (*b*) the pan or bucket; (*c*) the weights, consisting of silica rod or open tube in the form of hooks, making together a weight of about 24 mgrm.; these [(*a*), (*b*) and (*c*) together] were balanced by a single counterweight of quartz suspended from the opposite arm of the beam. The bulb had a capacity of 158·04 cu. mm., and at 15° and 760 mm. pressure it displaced 0·1937 mgrm. of air; hence a pressure change of 1 mm. is at this temperature equivalent to an alteration of weight of 0·000255 mgrm.

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* 'Roy. Soc. Proc.,' A, vol. 84, p. 538; see also Steele and Grant, *ibid.*, A, vol. 82, p. 580.

The weights ranged from 20 mgrm. down to 0·1 mgrm. and were approximately adjusted on a delicate assay balance to within 1/100 mgrm.; an operation which, on account of the volatility of silica at its melting-point, is fairly easy. The pieces were constructed of different shapes so that they could be readily distinguished from one another. The smaller weights were made of fine silica capillary tubing, open at one end. The accurate comparison of the weights with one another was carried out in the micro-balance itself with the help of the counterpoise-bulb E. One of the 0·1 mgrm. pieces was first weighed against the bulb; this necessitated a change of pressure of about 400 mm., and care was taken to eliminate errors due to temperature changes and consequent air currents. The true value of the 0·1 mgrm. weight being known, it was easy to standardise the other two 0·1 mgrm. weights, and by successive replacement, all the pieces in the set. The values of the silica weights were thus determined in terms of the air displaced by the bulb; and this was known with a high degree of accuracy, probably to 1 part in 2000; but for our purpose an error in the standard was of course immaterial.

It will be clear from what has been said that since the balance was constructed for a constant load, weighing was always carried out by substitution, and the weights and object to be weighed, as well as the bulb, were always on the same side of the balance beam. The small object was placed in the bucket G, and weights were then removed until equilibrium was nearly restored; exact balance was attained by closing the case and varying the pressure until the spot of light on the scale had been brought back to the null-point. Thus the weights served as a coarse, and the counterpoise-bulb as a fine adjustment.

Although a knowledge of the relative values only of our weights was important, it should, perhaps, be pointed out that the standard weight calculated from the air-displacement of the bulb is practically the same, whether the bulb is vacuous or contains air. A vacuous bulb, counterpoised in a vacuum, is balanced by its own weight of silica at the opposite end of the beam. In air the silica of the bulb and the silica balancing it are buoyed up equally, and the weight turning the beam is the weight of air equal in volume to the internal volume of the bulb. If the bulb contains air, and is balanced in a vacuum, the silica at the opposite end of the beam balances the silica of the bulb as well as the air in it. This excess of silica is, however, of so small a volume that the weight of air which it displaces is negligible, and in consequence the buoyancy of the bulb is hardly diminished from what it would have been had the bulb been vacuous.

Before the balance was used a considerable amount of time was spent in testing it. The zero-point was found to be perfectly constant. Without the counterpoise-bulb no change in zero was detectable with large changes of pressure within the case. The sensibility was such that a deflection of the zero-point by 1 scale-division corresponded to 0·000014 mgrm. The weights were calibrated three times, and the annexed table shows their value and the method of entering them in our note-book.

Weight.	Face value.	True value.	Weight.	Face value.	True value.
	mgrm.	mgrm.		mgrm.	mgrm.
	2	2·01955		0·2	0·20535
	1	1·01645		0·2	0·19034
	1	1·00776		0·1	0·13576
	0·5	0·50082		0·1	0·10737
	0·5	0·49243		0·1	0·11004

For calculating the air-displacement of the bulb, the formula given by Steele and Grant was used, viz.:—Change in weight of air displacing bulb $= V\sigma_0 T_0/P_0 \,.\, (P_1/T_1 - P_2/T_2)$, where V is the volume of the bulb; σ_0 the density of air at normal temperature and pressure, T_0 and P_0; P_1 and T_1 are the pressure and temperature of the air in the case when the beam is unloaded; and P_2 and T_2 when the beam is loaded. The expression

$V\sigma_0 T_0/P_0$ is a constant for the bulb, and in our experiments had the value 0·07340.

In comparing the weights of substances of density different from that of quartz, a correction has to be made for the variation of buoyancy of the substance itself, as the temperature and pressure change. If the substance is denser than silica, which was the case in our experiments, the change of air-displacement with pressure and temperature is of opposite sign to that of the counterpoise bulb. Knowing the density of the substance weighed, the correction can be readily calculated. If x represents the apparent change of weight per milligramme per atmosphere undergone by the substance when the air in the balance-case is at 0° C., then x is equal to the difference between the alteration in buoyancy of 1 mgrm. of quartz and the substance per atmosphere at 0°. If Δ_Q = the density of quartz, and Δ_S = the density of substance, and σ_0 = the density of air at 0° and 760 mm., then $(1/\Delta_Q - 1/\Delta_S)\sigma_0 = x$, from which x can be calculated. If the density of the substance is unknown, the value of x can be determined experimentally, and since Δ_Q and σ_0 are known, Δ_S can be calculated. To determine x the counterpoise-bulb is removed from the balance and replaced by a counterweight. After placing a known weight of substance in the pan the beam is exactly balanced by adding weights and small fragments of silica fibre. The shift of the zero-point for a known pressure-change is then determined, and the temperature measured. The substance is then removed, the counterpoise-bulb replaced, weights added to restore equilibrium, and the change of pressure necessary to cause the same zero-shift over the same part of the scale measured. In order to determine the magnitude of the vacuum correction of any substance of unknown density, it is therefore only necessary to determine x per milligramme per atmosphere at the mean temperature of the weighings, and since in most cases x is small, a slight error in its value has no important influence on the results.

To illustrate how x has been measured, and how an approximate value for the density of a substance can be arrived at by this method, we give the results of two experiments, one with very pure anhydrous radium chloride, and the other with the anhydrous bromide :—

Radium Chloride.—1·818 mgrm. of anhydrous salt placed in the bucket was found to cause a deflection in the zero-point corresponding to 39·4 divisions when the pressure was changed by 760 mm. at a temperature of 16·85°. The average value of one scale-division at this part of the scale was found to be 0·00001414 mgrm.; hence the change of buoyancy per atmosphere $= 39{\cdot}4 \times 0{\cdot}00001414 = 0{\cdot}000557$ mgrm. at 16·85°, and at 0°,

$0{\cdot}000557 \times 289{\cdot}85/273 = 0{\cdot}000591$ mgrm. The density of the silica from which the balance beam was made proved to be 2·197; the density of air at 0° and 760 mm. is 0·001293. Hence,

$$(1{\cdot}818/2{\cdot}197 - 1{\cdot}818/\Delta_S)\,0{\cdot}001293 = 0{\cdot}000591 \text{ mgrm.},$$

and $\Delta_S = 4{\cdot}91$. The vacuum correction per atmosphere per milligramme radium chloride is, therefore, at 16·85°, $0{\cdot}000557/1{\cdot}818 = 0{\cdot}000306$ mgrm.

By similar measurements, the density of anhydrous radium bromide was found to be 5·78, and the vacuum correction per milligramme per atmosphere at 18° equals 0·000342 mgrm. These values for the densities must, of course, only be taken as approximations.

To return to the fractionations. The five fractions were next treated in the following manner:—The contents of 2 were evaporated to crystallising point and the liquor transferred to 1 with the silica pipette, being added to the liquor already there. Similarly, the contents of 3 were evaporated and crystallised; its liquor was transferred to 2; the contents of 4 were treated similarly, and the liquor transferred to 3. The crystals in 4 were then dissolved in water, and the solution was transferred to 5; 4 was then washed three times, each time with a drop of water; and these washings were also transferred to 5. Capsule 4 was now empty; it was placed in position 1; 1 now became 2, 2 became 3, and 3, 4. The liquor in 2 was evaporated to crystallising point and cooled. Its liquor was transferred to the empty 1. The same process was repeated with 3, 4, and 5, their liquors being transferred to 2, 3, and 4. This constituted one "round."

After two such "rounds," a sample was taken for determination of equivalent. Weight of chlorides = 1·5830 mgrm.; of bromides = 2·0537 mgrm.; atomic weight = 228·2. It was suspected at this stage that some reaction must have taken place between the phosphoric anhydride through which the hydrogen bromide passed before entering the silica crucible, whereby a volatile phosphorus compound might have been formed, for it was noticed that on the lid of the silica crucible there were whitish spots. On dissolving this deposit off the lid with nitric acid a distinct yellow precipitate was formed with ammonium molybdate. The apparatus for preparing hydrogen bromide was therefore altered, so that the hydrogen was dried with pentoxide before bubbling through the bromine bottle; and the mixture of gases, after passage over red-hot asbestos, entered the silica crucible containing the radium bromide. In this way all danger of contamination of the bromide with phosphorus was avoided. Contamination with a phosphate would tend to raise the equivalent of radium, and might explain the high number obtained.

Recrystallisation was proceeded with until eight "rounds" had been achieved, and a sample was removed (1). The contents of capsule 5 were then dissolved in water to which a drop of hydrobromic acid had been added, and evaporated to crystallising point; it was arranged that only a couple of drops of mother-liquor remained with the crystals. This process was repeated, and a sample of these crystals was removed (No. 2). Again the crystals were redissolved as before, and a new crop obtained; this was repeated, and a sample of this crystallisation (No. 3) was preserved. A similar process, three times repeated, yielded sample 4, and a further crystallisation yielded sample 5. One more crystallisation gave sample 6, and one more, sample 7.

Samples 1 and 2 were reserved. Samples 3 and 4 gave the following figures :—

	Weight of bromide.	Weight of chloride.	Loss of weight.	Atomic weight.
	mgrm.	mgrm.	mgrm.	
Sample 3..................	1·50117	1·15474	0·34640	225·48
" 4..................	0·36910	0·28400	0·08510	225·90
" 5..................	Was accidentally spilt, so that no data are available.			
" 6..................	2·85262	2·19586	0·65676	226·40

This sample was transferred to a silica capsule, and the weighing-tube was washed out and re-weighed, in order to see that its weight had not changed.

The sample was then replaced, with small loss, some fragments of bromide being impossible to remove from the capsule. The ratio was again determined.

	Weight of bromide.	Weight of chloride.	Loss of weight.	Atomic weight.
	mgrm.	mgrm.	mgrm.	
Sample 6 repeated......	2·76084	2·12492	0·63592	226·25
After a second transference the figures were—				
" "	2·61099	2·00988	0·60110	226·35
After a third transference—				
" "	2·43281	1·87275	0·56006	226·35

This sample, it was thought, might have become contaminated with dust, leaving a siliceous residue on ignition; any unchangeable matter would have raised the atomic weight; the presence of any other impurity, non-volatile in hydrochloric or hydrobromic acid, but changed to chloride or bromide by their action, except thorium and uranium, would have lowered the atomic weight. The sample was dissolved in two drops of the purest "silica" water, and any possible impurities allowed to settle in a silica tube; it need hardly be said that no sediment was visible. The clear liquid was removed with a silica pipette, transferred to the weighing-tube, and saturated with gaseous hydrogen bromide. Radium bromide was precipitated in crystals, and the mother-liquor was removed with a silica pipette. The crystals were then dried and heated in hydrogen bromide until the weight became constant; they were then transformed into chloride, and again weighed.

	Weight of bromide.	Weight of chloride.	Loss of weight.	Atomic weight.
Sample 7..................	mgrm. 2·36062	mgrm. 1·81711	mgrm. 0·54351	226·45

Samples 1, 2, and 3 were next united, so as to check the earlier values; it will be remembered that sample 1 had been reserved.

	Weight of bromide.	Weight of chloride.	Loss of weight.	Atomic weight.
Samples 1, 2, and 3 ...	mgrm. 2·91458	mgrm. 2·24144	mgrm. 0·67302	225·20

The sample was then converted from chloride to bromide.

Weight of chloride.	Weight of bromide.	Loss of weight.	Atomic weight.
mgrm. 2·24113	mgrm. 2·91415	mgrm. 0·67302	225·17

Knowing the value for samples 1, 2, and 3 together, and knowing the value for 3, the value for samples 1 and 2 together was calculated. The facts may now be stated thus:—

Samples 1 and 2 gave the atomic weight by calculation...... 224·56
„ 1, 2, and 3 „ „ „ ...... 225·19
„ 3 „ „ „ ...... 225·48
„ 4 „ „ „ ...... 225·90
„ 6 „ „ (mean of 4) ...... 226·34
„ 7 „ „ ...... 226·45

The fractionation and rejection of 0·07 mgrm. of bromide between 6 and 7 has not materially altered the figure; it appears fair, therefore, to adopt the mean of samples 6 and 7 for the final atomic weight; this then becomes **226·36**.

This figure confirms Madame Curie's results, and is at variance with Hönigschmid's. The special interest in these determinations of atomic weight is that, as pointed out by one of the authors in his Presidential Address to the British Association, it affords for the first time a basis for approaching the difficult question of the ancestry and descent of the elements.

Assuming, first, that radium is the great-grandchild of uranium; second, that the only concomitant of the disintegration of these elements is helium; third, that each atom of uranium, during its change into uranium X, parts with two α-particles, *i.e.*, with two atoms of helium; and lastly, that the atomic weight of helium is 3·994 (Watson); it follows that the difference in atomic weight between uranium and radium should equal $3{\cdot}994 \times 3 = 11{\cdot}98$. This condition also involves the assumption that no considerable number, or rather weight, of β-particles escapes. Taking the atomic weight of uranium as 238·5, and subtracting 11·98, the figure 226·52 for the atomic weight of radium follows. On the other hand, assuming that Richards and Merigold* have given the only trustworthy series of determinations of the atomic weight of uranium, the mean of their two series is 238·41. Zimmermann's work, giving an atomic weight of 239·62,† may be disregarded; also that of Aloy, which is unfavourably criticised by F. W. Clarke. Now, subtracting 11·98 from 238·41, 226·43 appears to be the calculated atomic weight of radium, corresponding well with our figure, 226·36.

The radium series is supposed to terminate in lead, with evolution of five α-particles; and the atomic weight of lead is given in the official table of atomic weights as 207·1. But we should expect $226{\cdot}4 - 19{\cdot}92 = 206{\cdot}48$ for the atomic weight of lead. Clarke's general mean is 206·97; and, taking Baxter and Wilson's determinations, made in Richards' laboratory,‡ the figure is 207·08. The difference is no less than 0·6 of a unit. This is inexplicable on the assumptions made above. One of the following conclusions must therefore be drawn:—

(*a*) That lead is not the final disintegration product of radium. But there is no known element of atomic weight 206·5, and no place for it in the periodic table.

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* 'Amer. Acad. Proc.,' 1902, vol. 37, p. 365.

† 'Ann. Chem.,' 1886, pp. 232, 299.

‡ 'Amer. Acad. Proc.,' 1907, vol. 43, p. 365.

(*b*) That the atomic weights of radium and uranium are about 0·5 unit too low; this is not impossible, granting that the value 226·4, found by us, is only a minimum.

(*c*) That helium is not the only gaseous product of disintegration; such a possibility, if true, would, of course, render the calculation useless.

In the present state of our knowledge, redeterminations of the atomic weights of uranium and lead, especially of the former, would seem to be imperative. But, so far as the present state of our knowledge goes, it may be taken that the atomic weight of lead is probably fairly exactly known, and may be accepted as not far from 207. Adding to this 20, we have 227, a number considerably greater than that found for radium by us. But it must be remembered that our figure is to be regarded as a minimum one, because all likely impurities would lower the atomic weight.

Appendix.

It appears to us advisable to add some details dealing with the precautions taken in such work with the micro-balance, and also to reproduce some details illustrating the method.

The transformation of chloride into bromide and *vice versâ*, which served for the determination of atomic weight, has been described in outline in the earlier part of this paper. The process itself needs no special mention, but in the course of the researches it was found that certain precautions were essential when dealing with milligrammes and fractions of a mllligramme, which were altogether unnecessary when working with larger quantities of material.

In weighing the bromide in the small silica bucket, the greatest care had to be taken to exclude moisture, although with large quantities in a silica crucible, no special precautions were necessary. Again, in transferring the bucket containing the radium bromide from the heating crucible to the desiccator, varying quantities of moisture were absorbed, and the weights of the same sample after successive heatings often differed considerably. It was found essential to displace the hygroscopic hydrogen bromide by some inert gas before transference; and hydrogen was first tried. To our surprise we found that the salt, when heated in this gas, gradually lost weight, although no alteration in its appearance was observed. The use of pure nitrogen for this purpose proved quite satisfactory; and even when the radium salts were heated in it to bright redness for over an hour, no appreciable change in weight could be detected.

The procedure finally adopted both for chloride and bromide was to displace the halogen hydride from the heating crucible by pure nitrogen, to heat the salt for about five minutes in this gas, and to transfer the bucket and its contents, while still hot, to the desiccator. After it was cold, the transference to the balance was effected as quickly as possible, and the case was immediately pumped out. Owing to the presence of barium oxide in the balance-case, it acted as a vacuum desiccator, and moisture was completely excluded during the weighings.

Although it had been found that the weight of a silica crucible containing a radium salt remained perfectly constant within the limits of sensibility of an assay balance after prolonged exposure to hydrogen chloride or bromide at bright redness, careful experiments were made to see if any alteration whatever occurred when the bucket, after the same treatment, was weighed on the micro-balance. At first it appeared as if the bucket increased slightly in weight, but it was found that the gain was only apparent, and was caused in all probability by the deposition of fine particles of dust on the balance-beam, in spite of the careful filtering of the air entering the case. The zero of the balance, though as a rule perfectly constant, was found to be liable to change, after the case had been filled or emptied more rapidly than usual. The counterpoise-bulb, and the weights suspended from the same arm of the balance as the bucket, had a much greater surface than their silica counter-weight, and the deposition of dust-particles had thus the effect of increasing the apparent weight of any object weighed. With care in emptying and filling the case, this effect was negligibly small, but, in order to guard against the possibility of error, a silica tare, of nearly the same weight as the bucket, was constructed, and the pressure and temperature when the tare was balanced were always noted before carrying out a weighing. In this way, any shift in the zero-point of the balance between the weighings could be detected and allowed for. Subsequent experiments demonstrated the almost perfect constancy of weight of the silica bucket during the operations of an experiment.

The possible introduction of impurities into the salt during its conversion to chloride or bromide was carefully considered, but, on account of the gaseous nature of the substances effecting the transformation, possible sources of contamination were greatly restricted. The hydrogen chloride was evolved from pure "contact" sulphuric acid and solid ammonium chloride, and, after its passage through a tube filled with glass-wool, was led into the reaction-crucible. The nitrogen, prepared in the usual way, by leading a mixture of air and ammonia over red-hot copper, was stored in a large gas-holder over weak acid, and, before use, was passed again over red-hot copper, to eliminate the last traces of oxygen. It was dried by passage over concentrated sulphuric acid, and, finally, led through a tube packed with lumps of fused caustic soda. The hydrogen bromide, prepared as described at the beginning of this paper, was made from hydrogen evolved by the electrolysis of caustic baryta and very pure bromine. Calcium chloride was used to dry the hydrogen before its passage through the bromine, and the hydrogen bromide was freed from any traces of moisture by passage over anhydrous calcium bromide. The best proof, however, that the radium salt did not take up any impurities from the gaseous reagents lies in the fact that it was found possible, after converting the bromide to chloride, to reconvert the salt to bromide, and to recover the original weight almost exactly.

In carrying out a determination, the salt was always weighed after several successive treatings, until its weight ceased to change appreciably. Starting with the crystallised bromide, the salt was heated to redness in hydrogen bromide in the manner described, transferred to the balance, and its weight was determined approximately. It was then re-heated for half an hour, and an accurate weighing was made. This process was repeated until the weight became constant. The conversion to chloride was usually complete after a two hours' heating, and, after this, weighing to constant weight was carried out as before. Re-conversion to bromide required about four or five hours' heating. The weighings themselves were rather tedious, as it was found to be imperative to leave the balance for an hour, so as to allow of the establishment of complete temperature equilibrium before the readings were made.

We append a full calculation of the results of the weighings of sample 6.

	Zero reading.	Pressure corr. to 0°.	Temp.	Weight of air displaced by bulb.
			°	
Silica tare on balance	259	435·4	19·0	235·4 × 0·0734 /292·0 = 0·10945
Bucket on balance......	258	424·0	18·5	424·0 × 0·0734 /291·8 = 0·10666
Bucket and bromide (final weight)	257	108·6	18·3	108·6 × 0·0734 /291·3 = 0·02737
Bucket and chloride (final weight)	261	378·8	18·6	378·8 × 0·0734 /291·6 = 0·09536
Silica tare	257	435·8	19·0	435·8 × 0·0734 /292·0 = 0·10955

Weight of bromide:—

Weights used to balance bromide	2·51198	mgrm.
Weight added by bulb	−0·07929	„
Zero correction	+0·00001	„
Vacuum correction = 0·000342 mgrm. per atmosphere per milligramme = $108/760 \times 2{\cdot}43 \times 0{\cdot}000342$.................	+0·00011	„
	2·43281	„

Weight of chloride (since the tare has not altered appreciably in weight, the same weight for the empty bucket was taken):—

Weights removed to balance chloride	1·88379	mgrm.
Weight added by counterpoise-bulb, 0·10666 − 0·09536......	−0·01130	„
Zero correction, $3 \times 0{\cdot}000014$	−0·00004	„
Vacuum correction, $379/760 \times 1{\cdot}87 \times 0{\cdot}000306$	+0·00031	„
True weight of chloride	1·87276	„

Hence, change of weight on conversion, 2·43281 − 1·87276 = 0·56005 mgrm. The atomic weight is given by the equation, where 159·84 = Br_2, and 70·92 = Cl_2,

$$x + 0{\cdot}56006 = 1{\cdot}87276 \times 159{\cdot}84 - 2{\cdot}43281 \times 70{\cdot}92;$$

whence

$$x = 226{\cdot}35.$$

Details of the other experiments are set forth in the table appended. Finally, in case the radium results might have been affected by some constant error, the atomic weight of barium was determined in exactly the same manner as that of radium. Merck's guaranteed pure barium chloride, containing only a trace of alkalies, was recrystallised four times from pure distilled water. The salt was then precipitated by means of gaseous hydrogen chloride, recrystallised once more from pure water in a silica vessel, and a specimen taken for analysis. The results obtained were:—

	Weights added.	Air displaced.	Zero correction.	Vacuum correction.	True weight.	Atomic weight.
Barium bromide	3·52843	−0·02299	−0·00032	+0·00045	3·50557	137·37
„ chloride	2·51198	−0·05535	−0·00011	+0·00016	2·45668	137·32
„ bromide	3·52843	−0·02309	+0·00004	+0·00045	3·50583	

The International table for 1911 gives, for barium, the atomic weight 137·37; and these values are sufficiently close to prove that the method is free from any constant error.

Table.

		Weights removed.	Weights applied by pressure change.	Zero correction.	Vacuum correction.	True weight.	Weight difference. $RdBr_2-RdCl_2$.	Atomic weight.
		mgrm.				mgrm.		
Samples 1, 2 and 3 ...	Bromide	2 ·93802	−0 ·02401	+0 ·00014	+0 ·00043	2 ·91458	0 ·67314	225 ·2
	Chloride	2 ·24686	−0 ·00589	+0 ·00011	+0 ·00036	2 ·24144		
" 1, 2 and 3 ...	Bromide	2 ·93802	−0 ·02401	+0 ·00001	+0 ·00043	2 ·91415	0 ·67302	225 ·19
	Chloride	2 ·24686	−0 ·00617	+0 ·00008	+0 ·00035	2 ·24113		
Sample 3	Bromide	1 ·47944	+0 ·02201	0	+0 ·00028	1 ·50117	0 ·34640	225 ·48
	Chloride	1 ·13833	+0 ·01638	−0 ·00021	+0 ·00018	1 ·15474		
" 4	Bromide	0 ·44846	−0 ·07936	0	0	0 ·36910	0 ·08510	225 ·9
	Chloride	0 ·34109	−0 ·05738	+0 ·00028	+0 ·00001	0 ·28400		
" 6	Bromide	2 ·92863	−0 ·07616	+0 ·00003	+0 ·00012	2 ·85262	0 ·65676	226 ·40
	Chloride	2 ·22246	−0 ·02685	0	+0 ·00025	2 ·19586		
" 6	Bromide	2 ·83065	−0 ·06985	−0 ·00015	+0 ·00019	2 ·76084	0 ·63592	226 ·25
	Chloride	2 ·12692	−0 ·00249	+0 ·00014	+0 ·00035	2 ·12492		
" 6	Bromide	2 ·61935	−0 ·00868	−0 ·00014	+0 ·00046	2 ·61099	0 ·60110	226 ·35
	Chloride	2 ·01955	−0 ·01003	+0 ·00003	+0 ·00033	2 ·00988		
" 6	Bromide	2 ·51198	−0 ·07929	+0 ·00001	+0 ·00011	2 ·43281	0 ·56006	226 ·35
	Chloride	1 ·88379	−0 ·01130	−0 ·00004	+0 ·00031	1 ·87275		
" 7	Bromide	2 ·37622	−0 ·01579	−0 ·00019	+0 ·00038	2 ·36062	0 ·54351	226 ·45
	Chloride	1 ·88379	−0 ·06676	−0 ·00004	+0 ·00012	1 ·81711		